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METAL OXIDE ACYLATES

Abstract:

Abstract of GB1274718

1,274,718. Metal oxide acylates. J. RINSE. 1 July, 1969 [2 July, 1968; 11 Oct., 1968], No. 33109/69. Heading C2C. [Also in Divisions C3 and C4] Metal oxide acylates are prepared by reaction of (a) at least one metal component selected from polyvalent metals and oxides, hydroxides and carbonates thereof, with (b) at least one volatile monocarboxylic acid having from 1 to 5 carbon atoms and (c) at least one monocarboxylic acid having at least 7 carbon atoms (preferably the molar ratio of metal to monocarboxylic acid having at least 7 carbon atoms is at least 1:1) to produce a metal oxide acylate, wherein at least one valency of each metal atom derived from the metal component is satisfied by an acylate group and each of the remaining valencies is satisfied either by an oxygen atom which is attached to another metal atom or by an acylate group, which process includes distilling the product at a temperature of from 100 to 250 C., and during the distillation adding a liberating agent for the volatile monocarboxylic acid whereby to liberate said volatile acid and obtain a metal oxide acylate wherein at least 55 mole per cent of the acylate content is of monocarboxylic acid having at least 7 carbon atoms, the liberating agent being selected from one or more of water, steam, a volatile alcohol, an aluminium alkoxide wherein each alkoxide group has at most four carbon atoms, a titanium alcoholate, wherein each alcoholate group has at most four carbon atoms, and a condensed titanium silicon alkoxide, wherein each alkoxide group has at most four carbon atoms, the amount of aluminium alkoxide, titanium alcoholate or condensed titanium silicon alkoxide used being not greater than 10% by weight of the metal oxide acylate product. In the above process, reactants (a) and (b) may be replaced by at least one salt 1795 of a polyvalent metal and a volatile monocarboxylic acid having from 1 to 5 carbon atoms. Novel compositions comprise a metal oxide acylate having at least two metal atoms other than aluminium bound to each other through an oxygen bridge and in which each metal atom has a valence number of at least two and is bound only to oxygen atoms and at least 55 mol. per cent of the acylate content is derived from monocarboxylic acid having at least 7 carbon atoms, the remainder of the acylate if any being derived from monocarboxylic acid having less than 7 carbon atoms, the molar ratio of metal to acylate in the composition being in excess of 1:1, and the excess metal being in a finely divided, stable, dispersed state as metal oxide are prepared by the above process if excess metal oxide (a) is used. Novel liquid (metal oxide acylate)/(metal alkoxide) reaction products, the metal oxide acylate having at least two metal atoms other than aluminium bound to each other through an oxygen bridge and in which each metal atom has a valence number of at least two and is bound only to oxygen atoms and at least 55 mol. per cent of the acylate content is derived from monocarboxylic acid having at least 7 carbon atoms, the remainder of the acylate if any being derived from monocarboxylic acid having less than 7 carbon atoms, the metal alkoxide comprising at most

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(54) METAL OXIDE ACYLATES

(71) I, JACOBUS RINSE, a Dutch subject, of 77 Anderson Road, Bernardville, New Jersey, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing metal oxide acylates and to certain novel metal oxide acylates which may be prepared by the method.

Although aluminium and titanium alcoholates have been reacted with organic acids or with metal acylates to form corresponding metal-oxide-acylates (MOA), which are either (a) cyclic trimers (OAlX)₃, (b) cyclic tetramers (X₄Ti₂O₆) or (c) linear compounds with di-, tri- and/or tetravalent atoms, such as



known processes are generally limited to metals which can form metal alcoholates or, as referred to by Turner et al. (United States Patent Specification No. 3,296,242), alkoxides or aryloxides, and/or fail to minimize any lower acyl substituent in the obtained product.

According to the present invention there is provided a process for preparing a metal oxide acylate by reaction of (a) at least one metal component selected from poly valent metals and oxides, hydroxides and carbonates thereof, with (b) at least one volatile monocarboxylic acid having from 1 to 5 carbon atoms and (c) at least one monocarboxylic acid having at least 7 carbon atoms to produce a metal oxide acylate wherein at least one valency of each metal atom derived from the metal component

is satisfied by an acylate group and each of the remaining valencies is satisfied either by an oxygen atom which is attached to another metal atom or by an acylate group, which process includes distilling the product at a temperature of from 100 to 250°C, and during the distillation adding a liberating agent for the volatile monocarboxylic acid whereby to liberate said volatile acid and obtain a metal oxide acylate wherein at least 55 mole % of the acylate content is of monocarboxylic acid having at least 7 carbon atoms, the liberating agent being selected from one or more of water, steam, a volatile alcohol, an aluminium alkoxide wherein each alkoxide group has at most four carbon atoms, a titanium alcoholate wherein each alcoholate group has at most four carbon atoms, and a condensed titanium silicon alkoxide wherein each alkoxide group has at most four carbon atoms, the amount of aluminium alkoxide, titanium alcoholate or condensed titanium silicon alkoxide used being not greater than 10% by weight of the metal oxide acylate product.

Preferably, the molar ratio of metal to monocarboxylic acid having at least 7 carbon atoms is at least 1:1.

In a modification of the process, the combination of metal component and volatile monocarboxylic acid may be replaced by a salt of the polyvalent metal and volatile monocarboxylic acid.

Further according to the invention there is provided a novel class of metal oxide acylate having at least two metal atoms other than aluminium bound to each other through an oxygen bridge and which has a formula selected from

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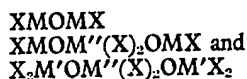
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where each X is an acylate group, each M is a divalent metal atom, each M' is a trivalent metal atom and each M'' is a tetravalent metal atom, and at least 55 mole % of the total acylate content of the compound is derived from carboxylic acid having at least 7 carbon atoms, the remainder, if any, being derived from carboxylic acid having less than 7 carbon atoms. In one preferred embodiment, the metal component of the metal oxide acylate comprises at least 2 metals of different valence numbers and at least 70 % of the total acylate content is derived from carboxylic acid having at least 7 carbon atoms.

Certain other metal oxide acylates illustrated in the Examples are also novel and form subsidiary embodiments of the invention.

In yet another embodiment of the invention are provided novel compositions obtained when the ratio of metal to monocarboxylic acid having at least 7 carbon atoms in the process exceeds 1:1. These compositions comprise a metal oxide acylate having at least two metal atoms other than aluminium bound to each other through an oxygen bridge and in which each metal atom has a valence number of at least two and is bound only to oxygen atoms and at least 55 mol percent of the acylate content is derived from monocarboxylic acid having at least 7 carbon atoms, the remainder of the acylate, if any, being derived from monocarboxylic acid having less than 7 carbon atoms, the molar ratio of metal to acylate in the composition being in excess of 1:1, and the excess metal being in a finely divided, stable, dispersed state as metal oxide.

MOAs of most metals which have a valence number in excess of one can be prepared by the process of the invention. They may be prepared from a metal, metal oxide, metal hydroxide or metal carbonate. One or more of these is reacted with a mixture of volatile (having from one to five carbon atoms) and non-volatile (having at least seven, and preferably from 9 to 22, carbon atoms) monocarboxylic acids, the mole ratio of metal to non-volatile acid being at least 1:1. The reaction proceeds by heating the reactants until all of the metal or metal compound has gone into solution and includes the step of distilling the product at a temperature of from 100 to 250°C and during the distillation step adding the specified liberating agent.

Instead of starting with one of the noted metals or compounds thereof, an acylate (of a volatile monocarboxylic acid, preferably formate or acetate) of a metal having a valence number of at least 2 (preferably 2 to 4) can be employed for this purpose. Such acylate is heated with a non-volatile carboxylic acid with the same preference for ratio of metal

to non-volatile acid as previously indicated and the remaining procedures effected as described. The metal acylate of a volatile monocarboxylic acid can, alternatively, be formed *in situ* and the non-volatile acid added directly thereto (without separation) to complete the reaction.

Chemically bound water of, e.g. metal acetates, assists in the liberation of (in such case) acetic acid from the desired product (MOA). Such acetic acid is then distilled off. In accordance with one embodiment of the invention water and/or steam is added during distillation as the liberating agent to liberate the volatile monocarboxylic acid. In the absence of chemically bound water, a larger quantity of water must be added to promote said liberation. Virtually all acylate groups of volatile acids, e.g. formate and acetate groups, should preferably be removed to produce MOA according to this invention because they adversely affect the properties of the end-products by increasing viscosity and melting points and decreasing solubility in organic solvents.

The acylate (X) of the MOA is thus essentially an acylate of a non-volatile monocarboxylic acid i.e. acid having at least 7 carbon atoms. It is preferably aliphatic with a completely hydrocarbon residue, i.e., in an acid Y-COOH, Y is entirely hydrocarbon.

In addition to providing a method with an increased range of available starting materials a further material contribution is the provision of a method for removing residual volatile acylate, e.g. acetate, groups from the produced metal oxide acylate. This is effected by one or a combination of the following steps:

1. Add water or steam slowly during distillation at 100° to 250°C. Some metals, such as mercury and copper, require lower temperatures (100° to 150°C) than others, such as iron and chromium. (The addition of water or steam is halted when no more acetic (or other lower alkanolic volatile) acid is noticeable in the distillate.)
2. Add a volatile alcohol, such as a lower alkanol, e.g. isopropanol and butanol, during the distillation (in lieu of or in addition to water or steam). The volatile alcohol reacts with residual volatile acylate, e.g. acetate, groups (yielding volatile ester) and couples the metal atoms by oxygen bonds.
3. Add a small amount, e.g. from 1 to 10 percent by weight (based on the total weight of MOA) of aluminium alcoholate, titanium alcoholate or condensed titanium silicon alkoxide. (The alcoholate or alkoxide is preferably one with at most 4 carbon atoms, e.g., isopropoxide or butoxide.) More than 10 percent by weight, e.g. up to 25 percent by weight, is needed for antimony and bismuth and bismuth oxide acylates, which are non-drying liquids. Otherwise, 10 percent or less is adequate to eliminate

residual lower acylate, e.g. acetate, and any excess thereof causes undesirable alkoxy groups in the final product. Silicon alkoxide delays or prevents drying, while aluminium alkoxide hydrolyzes in air; both effects are undesirable in most cases.

Scheme 1 is preferred. The reaction temperature for schemes 2 and 2 is at least 150°C and preferably from 170° to 200°C. Sometimes, as is the case with ferrous oxide tellate, water and alcohol are added alternatively to prevent solidification of the batch. Scheme 3 leads to a different product than schemes 1 and 2, but such product is closely analogous. The products of Scheme 3 can be maintained in liquid state at room temperature, whereas the products of schemes 1 and 2 are ordinarily solids (under the same conditions) which readily dissolve in such solvents as mineral spirits, turpentine and xylene.

A further aspect of the invention concerns the molar ratio of metal to non-volatile monocarboxylic acid. As said ratio is increased above 1:1, e.g. to 2:1 or 3:1, finely divided metal oxide is formed *in situ* in the product. Said finely divided metal oxide is in such a minute state or sub-division that it does not settle, but remains dispersed in the MOA, producing a fine paint with a high metal content without having to grind or to mill the pigment.

The metal which forms an integral part of the MOA must exist in the MOA in a form which has a valence number in excess of one. Said metal is an element or a plurality elements. When more than one metal is employed in the preparation of the MOA, the selected metals may, but need not, have the same valence numbers.

The metal is, e.g., calcium [II], magnesium [II], strontium [II], barium [II], zinc [II], cadmium [II], nickel [II], mercury [II], copper [II], iron [II] or [III], chromium [II] or [III], manganese [II] or [III], cobalt [II], aluminium [III], antimony [III], zirconium [IV], bismuth [III], cerium [III], titanium [IV], tin [II] or [IV] or lead [II] or [IV]. [Illustrative valence numbers of each of the enumerated metals in MOA are indicated in brackets following the respective metals.]

In order to prepare MOA according to this invention the metal itself can be employed as a suitable starting material. When so employed, it is preferred to have the metal in a finely divided state, such as in powder form. Iron powder, e.g., can be refluxed with aqueous acetic acid and the product reacted with tall oil fatty acids to produce ferrous oxide tellate.

The starting material is, alternatively, a metal compound, such as a metal oxide, e.g. chromium trioxide [CrO₃] or lead oxide [PbO], a metal hydroxide, e.g. calcium hydroxide [Ca(OH)₂] or aluminum hydroxide [Al(OH)₃], a metal carbonate, e.g. man-

ganese carbonate [MnCO₃] or lead carbonate [PbCO₃], or a metal acetate, e.g. basic iron acetate [Fe(OH)(OOCCH₃)₂] or titanium tetraacetate [Ti(OOCCH₃)₄].

The volatile carboxylic acids having 1 to 5 carbon atoms include propionic acid and butyric acid, but formic acid and acetic acid (particularly the latter) are preferred. The non-volatile monocarboxylic acids (i.e. having at least 7 carbon atoms) include such aliphatic acids as straight chain acids, e.g. stearic acid; branched chain acids, e.g. 2-ethylhexoic acid and isostearic acid; saturated acids, e.g. palmitic acid; and unsaturated acids, e.g. oleic acid and linoleic acid; such cycloaliphatic acids as naphthenic acids, and such aromatic acids as rosin (abietic acid). Where it is desired to obtain liquid products or low melting point solids, virtually the only limitation on the non-volatile monocarboxylic acid is that the MOA obtained therewith be fluid, or be readily soluble in paint or varnish solvents, e.g. mineral spirits, xylene or turpentine, to form compositions having a paint-like or more fluid consistency. The non-volatile carboxylic acid need not be a single acid, but can be a mixture of such acids, such as "Neo-Fat" products ("Neo-Fat" No. 1—56, "Neo-Fat" No. 1—54, "Neo-Fat" No. 1—60, "Neo-Fat" No. 3—R, "Neo-Fat" No. 11, "Neo-Fat" No. 17 and "Neo-Fat" S—142), coconut oil fatty acids and tall oil fatty acids.

The liquids or relatively low melting solids that form liquid compositions that may be obtained by the process of this invention can be converted into hard, heat-stable, adherent protective coatings on both metal and non-metal surfaces. Said products are low in cost; protective coatings prepared from the colored MOA do not bleach and are light-fast. The color is permanent in those products which are colored. These properties are inherent in the products without having to combine them with resins or other polymers or condensates. Color and binder are chemically combined. Said products also include stabilizers and catalysts.

Some MOA, such as those of zinc, lead, aluminium, antimony, titanium, zirconium and mercury, are nearly colorless; others, such as those of ferric iron (brown), ferrous iron (black), copper (green), chromium (green), nickel (green), and manganese [III] (brown), have color.

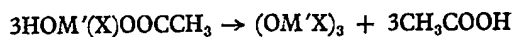
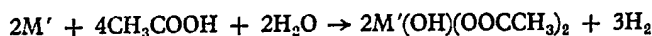
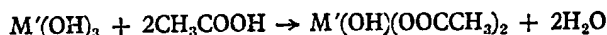
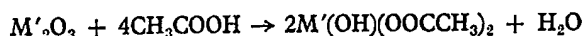
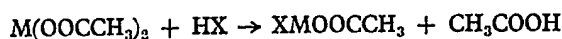
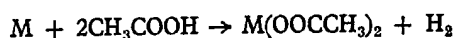
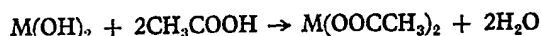
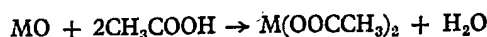
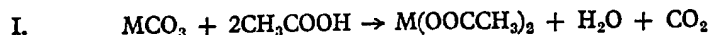
The removal of acylate groups derived from the volatile monocarboxylic acids from produced metal oxide acylate was a problem. As these groups increase the viscosity and the melting point of the metal oxide acylate, their presence is a detriment to the product. Although complete removal of such lower acylate groups is not possible when metals such as zinc and lead are employed, i.e., without precipitation of insoluble metal oxide, practically all of said lower acylate may be removed from most MOA by the process of the subject in-

vention. Other metals, such as iron and chromium, may be completely separated from lower acylate, e.g. acetate, groups by the methods herein taught. Even for lead and zinc oxide acylates at least 55 mol percent of the acylate groups are those of the non-volatile monocarboxylic acid.

For the formation of the MOA and the removal of lower acylate no solvent is required, e.g., when the metal is lead or zinc; the presence of other metals, however, may necessitate limited quantities of a solvent, such as mineral spirits (boiling point range 150° to 170°C),

turpentine or xylene (*o*-, *m*-, *p*-, or any mixture thereof), to maintain the MOA in a liquid state during distillation. However, as soon as most of the volatile acid has been removed, all MOA are liquids (indicating the absence of hydrogen bonds and the virtual absence of low molecular acylates) or are readily soluble in hydrocarbon solvents to form liquid compositions.

Using *M* to designate a divalent metal element; *M'*, a trivalent metal element; and *M''*, a trivalent metal element, typical reaction schemes follow:



wherein *X* is acyl of a non-volatile monocarboxylic (preferably aliphatic) acid;

R is either a hydrogen atom, lower alkyl, e.g. isopropyl, or lower acyl, e.g. acetyl.

In the preceding reaction schemes each *M*, *M'* or *M''* can represent a plurality of metal elements having the same valence number. Acetic acid is used solely as an exemplary volatile monocarboxylic acid. The list of reactions is not exhaustive and is not intended to be; it is merely illustrative. Other combinations, e.g. with tetra- and divalent metals [*XMOM''*(*X*)*OMX*] and with tetra- and trivalent metals [*X₂M'OM''*(*X*)*OM'X₂*], are also obtainable by the process of the subject invention.

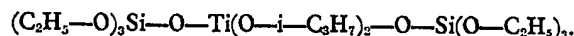
Wherever the mol ratio of metal to non-volatile acyl is ordinarily 1:1 and it is advantageous to obtain a product with a higher metal content, e.g. for paints, said mol ratio can be increased to 2:1, 3:1 or even higher. The reactions proceed in the same manner to yield MOA of the same formulae, but the

excess metal is highly dispersed in the MOA as metal oxide particles of such fineness that they do not settle; coatings prepared from MOA having such excess metal oxide content dry to a high gloss. Like principles are applicable to other mol ratios. Increasing the molar ratio of metal to non-volatile acylate thus results in a simple method of preparing paints without grinding. Such a product from copper, e.g. cupric oxide tellate (*TCuOCuT*) having cuprous oxide dispersed therein, is useful as an anti-fouling paint. When an excess of iron is employed in the preparation of ferric oxide ferric oxide tellate [*(OF₂FeT)₃*], a red-brown paint is obtained; this paint adheres strongly to aluminum metal, in particular, flakes forming an imitation gold paint.

MOA reacts with organic acids, such as mono- and dicarboxylic acids, e.g. maleic and

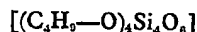
acetic acids, to form solids. Those MOA which are colored are dyes. MOA reacts with inorganic acids, e.g. sulfuric acid, to form soaps and is thus useful as an acid-binding agent; it reacts with alcohols and form solutions; it reacts with phenols, e.g. pentachlorophenol, to form products which are useful for, e.g., fungicides; and it reacts with sulfur to form products which are useful for, e.g., preparing high-viscosity polymers.

The preparation of relatively inexpensive imitation gold paint or ink is another facet of the subject invention. This is accomplished, e.g., by admixing ferric oxide tellate [(OF₂T)₃], such as that obtained according to Example 15, with aluminum flake, preferably a product with a monomolecular layer of stearic acid on the aluminum flake as is commercially available. The aluminum flake is employed in its marketed form, the stearic acid contributing materially to the value of the paint product.

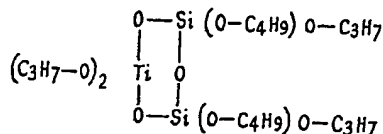


Method 2

Mix 284 g of TPT with 250 g of tetrameric silicon oxide butoxide



and promptly heat the resultant mixture to 120° C to obtain a clear liquid reaction product having a cyclic structure, such as:



The clear liquid is a colorless condensate which dries in air to a smooth coating and has greater stability with respect to temperature and hydrolysis than the reactants from which it is prepared. The condensate is useful as primers for protective coatings or as adhesion coatings for solid substrates.

Heating to 50° C results in a similar condensate.

The following examples illustrate representative embodiments of the subject invention and include both products and the manner in which said products are prepared. However, it is to be understood that the examples are intended solely for the purpose of illustration and in no way limit the scope of the invention which is defined in appended claims.

There is now described the production of certain liberating agents suitable for use in the process of the invention.

Method 1

Mix 284 grams (g) of titanium tetraisopropoxide (TPT) with 300 g of condensed ethylsilicate 40 (containing 40% SiO₂). The temperature rises 20° C, and a clear stable, colorless liquid, which does not form an insoluble skin or crust in the neck of the container results. This liquid is a compound of the formula:

Method 3

Mix 568 g of TPT with 150 g of condensed ethylsilicate and promptly heat the resultant mixture to 100° C. There is thus obtained a liquid oligomer of titanium and silicon wherein each silicon atom is linked to a titanium atom through an oxygen bridge. The liquid oligomer has a lower rate of hydrolysis than TPT and is useful as a catalyst in the preparation of silicon oxide alkoxide oligomers.

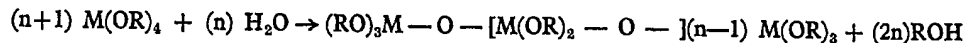
Method 4

Mix 568 g of TPT with 150 g of regular ortho-ethylsilicate. Drop water slowly into the admixture while heating same to a temperature of from 100° to 120° C to obtain a condensate which is an oligomer of silicon and titanium wherein each atom of silicon is bonded to a titanium atom through an oxygen bridge.

Method 5

Mix 182 g of condensed TPT with 208 g of ortho-ethylsilicate. Heat the resultant to a temperature of from 100° to 120° C to obtain a condensate having a structure with alternating —SiO— and —TiO— groupings.

The condensed TPT is prepared by mixing water with TPT and heating the resultant at a temperature of from 100° to 120° C according to the reaction scheme:



where M is titanium,

R is isopropyl, and

n is the number of moles of water reacted with (n+1) moles of titanium alkoxide.

Method 6

Heat a mixture of 145 g of titanium oxide butoxide $[(C_4H_9O)_2Ti_2O_6]$ prepared according to the disclosure of USP 3,087,949] and 206 g of silicon tetraethoxide (b.p. 165° C) to 50° C to obtain a colorless liquid which can be heated to 200° C without decomposition or distillation. The colorless liquid is comprised of compounds which are silicon/titanium oxide esters wherein silicon and titanium atoms are linked only through oxygen bridges. Cyclic oligomers, primarily tetrameric, predominate although some linear oligomer is present.

EXAMPLE 1

Heat an admixture of 30 grams (g) of antimony triacetate, 56 g of tall oil fatty acid and 10 g of mineral spirits to 200° C. Apply a vacuum (5 mm Hg) to the resultant mixture and allow the temperature to be lowered to 130° C, at which point add thereto 12 g of the product of Method 1 before raising the temperature to 170° C. Distill off ethyl and isopropyl acetates slowly. Apply a vacuum. There is thus obtained a clear light brown liquid which is useful as a catalyst for the preparation of urethane resins.

EXAMPLE 2

Heat a mixture of 30 g of antimony triacetate and 56 g of tall oil fatty acid to 210° C and apply a vacuum to the resultant mixture. After cooling same to 100° C, add thereto 12 g of a mixture of equal parts by weight (pbw) of titanium isopropoxide (TPT) and condensed ethylsilicate before heating again to 190° C. A liquid oil is thus obtained.

EXAMPLE 3

Reflux 25.5 g of bismuth carbonate $[Bi_2O_3 \cdot CO_2]$ with 40 g of acetic anhydride. Add thereto 36 g of 2-ethylhexoic acid, and raise the temperature of the resultant mixture to 210° C before applying a vacuum. Cool the reaction mixture to 100° C, and then add thereto 20 g of the product of Method 1. Raise the temperature to 130° C for ten minutes and then apply a vacuum. Distil off a mixture of ethanol and isopropanol. The residue is a clear brown liquid.

EXAMPLE 4

Heat a mixture of 40.6 g of bismuth triacetate and 56 g of tall oil fatty acid to 210° C and apply a vacuum to the resultant mixture. After cooling same to 100° C, add thereto 12 g of a mixture of equal parts by weight (pbw) of titanium isopropoxide and condensed ethylsilicate before heating again to 190° C. A dark colored liquid is thus obtained.

EXAMPLE 5

Dissolve 20 g of zinc oxide $[ZnO]$ in a mixture of 43 g of 2-ethylhexoic acid and 6 g of acetic acid. Heat the resulting ad-

mixture to 220° C and apply a vacuum thereto. Heat to 150° C before adding thereto 5 g of the product of Method 1. Thereafter further heat to a temperature of from 170° to 180° C for 40 minutes and apply a vacuum again to obtain a viscous liquid.

EXAMPLE 6

Heat a mixture of 28.6 g of basic ferric acetate, 24.3 g of zinc oxide $[ZnO]$, and 84 g of tall oil fatty acid to 200° C and, after subjecting the resultant mixture to a vacuum, add thereto 10 g of the silicon titanate product of Method 1. Thereafter apply a vacuum again to obtain a clear dark brown liquid which is useful as a preservative stain for lumber.

Replacing the product of Method 1 with an equivalent of each of the products of Methods 2 through 6 results in the preparation, in similar manner, of a liquid which is likewise useful as a preservative for lumber.

EXAMPLE 7

Dissolve 25.5 g of barium acetate in 40 g of water at 100° C, and add 74 g of 2-ethylhexoic acid to the resulting solution before heating same to 200° C. At the latter temperature add 12.6 g of bismuth carbonate and maintain for 30 minutes, whereupon the resulting batch becomes clear. Apply a vacuum and cool to 110° C before adding thereto 9 g of the product of Method 1. Thereafter heat to 130° C and apply a vacuum to remove liberated alcohols. There is thus obtained 117 g of a viscous clear oil which is useful as a stabilizer for plastics, e.g. vinyls, against heat.

The products of Examples 1 to 7 are liquids which are useful as protective coatings for solid substrates, e.g. wood. They are also useful as intermediates for paint driers, stains, catalysts, stabilizers and preservatives.

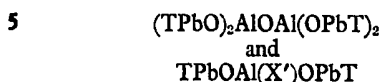
EXAMPLE 8

Heat a mixture of 84 g of isostearic acid and 12 g of acetic acid to 50° C prior to adding 12.8 g of cadmium oxide and 8.1 g of zinc oxide $[ZnO]$ thereto. Raise the temperature of the resultant mixture to 140° C, at which temperature clarification takes place. Thereafter add 14.8 g of aluminum formoacetate thereto; this also goes into solution at the latter temperature. Raise the temperature to 200° C and add 20 g of water thereto. Then apply a vacuum. The clear liquid which remains solidifies below 100° C. The composition is of the formula $XZnOAl(X)OCdX$ where X is isostearate and is a stabilizer for plastics.

EXAMPLE 9

Heat a mixture of 56 g of tall oil fatty acids, 6 g of acetic acid and 14.8 of aluminum formo-acetate to 50° C, and add thereto 44.6 g of litharge and 15 g of mineral spirits. The resulting batch clarifies on heating same to 200° C. Add 30 g of butanol at that tempera-

ture and continue heating to 235° C before applying a vacuum. A greyish product is obtained which is a solid at 50° C. Said product is a mixture of compounds of the formulae:



wherein T is tall oil fatty acid radical and X' is acetoxy.

10 EXAMPLE 10

At 60° C mix 114 g of an isopropanolic solution of titanium acetate (containing 9.6 g of titanium) with 53 g of stearic acid. Distil the resultant mixture to remove solvents until 150° C is reached. At 150° C drop 10 g of water into the distilland slowly in order to remove residual acetate groups. Apply a vacuum (5 mm Hg) at 180° C. A wax which is clearly soluble in hexane and which has a melting point of 40° C is thus obtained. The wax is useful for waterproofing.

EXAMPLE 11

Distil a mixture of 83 g of a butanolic solution of tin tetraacetate (23.6 g of tin) and 30 g of 2-ethylhexoic acid. Drop 5 g of water slowly into the distilland at 130° C. Apply a vacuum at 180° C. There is thus obtained a viscous liquid which is useful as a catalyst for the preparation of urethane foams.

30 EXAMPLE 12

Heat 150 g of an isopropanolic solution of zirconium acetate (18.2 g of zirconium) with 56 g of oleic acid and 60 g of mineral spirits. While maintaining at 200° C, drop water into the batch until it begins to become turbid (about 50 g). Apply a vacuum and continue heating until a temperature of 260° C is reached. A light brown solid product, which is soluble in xylene, is thus obtained. The product is useful as a drier for oil paints.

EXAMPLE 13

Heat 38.2 g of basic iron acetate [$\text{HOFe}(\text{OOCCH}_3)_2$] with 28 g of tall oil fatty acid to a temperature of 220° C. Then drop 25 g of water slowly into the resultant mixture at that temperature. Apply a vacuum. There is thus obtained a reddish brown resinous mass which, upon addition thereto of 30 g of either mineral spirits or turpentine, yields a bright brown paint which dries to a hard glossy coating. The ferric oxide tallate produced has the formula $(\text{OFeT})_3$.

Replacing the basic iron acetate with 40 g of cupric acetate and otherwise following the identical procedure yields cuprous oxide dispersed in copper oxide tallate (TCuOCuT) which, upon dissolving in one of the noted solvents, is useful as a rapid drying brown anti-fouling paint.

Copper oxide tallate is an interesting material. When prepared below 150° C, it is green and dries slowly to a clear green film; but when prepared at 200° C, it is brown and dries rapidly to a clear green coating. If excess copper is used and the product contains Cu_2O , its color is brown and it dries to a brown coating.

EXAMPLE 14

Heat a mixture of 56 g of tall oil fatty acids, 24 g of acetic acid, 40 g of mineral spirits or xylene and 41.2 of cupric hydroxide [$\text{Cu}(\text{OH})_2$] to 140° C. Drop 100 g of water slowly into said mixture while maintaining the stated temperature. Then heat further to 190° C. [Intermittently mineral spirits and xylene (a total of about 30 g of each) are added to maintain the mixture in the liquid state and for the reduction of cupric oxide to cuprous oxide. The color of the batch, which was initially green, turns brown.] Continue heating of 230° C. Apply a vacuum at the latter temperature until distillation stops. A brown xylene-soluble solid is thus obtained. Xylene solutions of said solid dry in air to dichromatic coatings with good gloss and are useful as anti-fouling paint for ship bottoms.

EXAMPLE 15

Reflux 22.4 g of iron powder with 80 g of acetic acid and 80 g of water until no more hydrogen comes off. Distil off water and excess acid while slowly adding 40 g of mineral spirits and 56 g of tall fatty acids to the distilland, which forms a deep black solution. While maintaining the temperature at 200° C, add 100 g of water and 10 g of isopropanol to the distilland to remove residual acetate groups. Apply a vacuum to the resultant mixture at 220° C. A black solid is thus obtained. Said solid (84 g) dissolves in 30 g of xylene and 10 g of butanol to form a black paint which dries to a high gloss and is suitable as an anti-corrosive. The suspended iron oxide does not settle during storage.

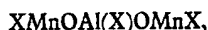
EXAMPLE 16

Heat 14.8 of aluminium acetate-forming [$\text{HCOOAl}(\text{OH})\text{OOCCH}_3$] together with 16.2 g of zinc oxide and 50 g of water. After 5 g of water have been distilled off, add 53 g of stearic acid and 30 g of mineral spirits to the resultant mixture and continue heating to 180° C, at which temperature the batch becomes clear. While maintaining the temperature, add 10 g of water slowly to said batch. Heat further to 200° C and apply a vacuum at the latter temperature. The compound of the formula $(\text{XZnO})_2\text{AlOAl}(\text{OZnX})_2$ is thus obtained [X is stearate]. This compound is useful as a rubber compounding additive.

EXAMPLE 17

Heat 24.5 g of crystalline manganese acetate with 3.9 g of freshly prepared aluminium hy-

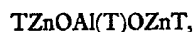
droxide and 60 g of mineral spirits. At 130° C add thereto 28 g of stearic acid. Add a further 14 g of stearic acid thereto at 175° C. Thereafter add 50 g of hydrocarbon solvent Isopar M. "Isopar" is a Registered Trade Mark. The batch becomes clear at 200° C and gradually liquefies at 230° C. Add 10 g of water and apply a vacuum thereto. The product is a dark brown solid wax soluble in butanol and mineral spirits and of the formula



wherein X is stearate.

EXAMPLE 18

Heat 22 g of crystalline zinc acetate with 3.9 g of aluminium hydroxide and 5 g of water. Add 28 g of tall oil fatty acids thereto at 130° C and an additional 14 g thereof at 180° C. Apply a vacuum. Add 10 g of water slowly to the resultant mixture. Then heat the obtained batch to 200° C and distill *in vacuo* to obtain a clear oil which dries to a clear film after addition of 0.5 g of cobalt drier. The product is of the formula



wherein T is the residue of tall oil fatty acids.

EXAMPLE 19

Heat 14.8 g of aluminium acetate-formate $[\text{HCOOAl(OH)OOCCH}_3]$ together with 11.6 g of magnesium hydroxide and 50 g of water. After 5 g of water has been distilled off, add 53 g of stearic acid and 30 g of mineral spirits to the resultant mixture and continue heating to 180° C, at which temperature the batch becomes clear. While maintaining the temperature, add 10 g of water slowly to said batch. Heat further to 200° C and apply a vacuum at the latter temperature. The compound of the formula



is thus obtained [X is stearate].

EXAMPLE 20

Heat 7.2 g of aluminium acetate-formate with 14 g of isostearic acid and 20 g of mineral spirits to 180° C. While maintaining that temperature, add thereto 15 g of water. Raise the temperature to 220° C under vacuum. The resulting compound is of the formula $(\text{OAlX})_3$, wherein X is isostearate.

EXAMPLE 21

Distil a mixture of 24.7 g of chromium acetate, 15 g of butanol and 35 g of water. During distillation, add to the distilland 30 g of butanol, 20 g of xylene and 28 g of isostearic acid. When the temperature of the

distilland reaches 160° C, add 20 g of Isopar M ("Isopar" is a Registered Trade Mark) hydrocarbon solvent thereto and then apply steam distillation. Raise the temperature to 240° C, whereupon acetic acid is formed and is removed under vacuum. The product is cyclic chromium oxide isostearate $(\text{OCrX})_3$ [n is predominantly in integer from 3 to 5, primarily 3], which is a solid melting above 150° C and soluble in xylene. Xylene solutions have a clear, bright, intense green color.

EXAMPLE 22

Heat 38 g of ferric acetate with 26 g of neoheptanoic acid and 30 g of Isopar M hydrocarbon solvent to 240° C. While maintaining the batch at that temperature, add thereto 15 g of water. Then place under 2 cm of Hg vacuum until distillation terminates. The obtained dark brown liquid solidifies on cooling to a black solid (cyclic iron oxide heptanoate) which is soluble in equal parts by weight of a 2:1 xylene-butanol mixture.

EXAMPLE 23

Heat to 240° C a mixture of 19.1 g of basic iron diacetate, 29.5 g of methyl linoleate and 10 g of mineral spirits and maintain that temperature for 60 minutes (until foam formation ends). While maintaining the temperature, add thereto 10 g of water. Apply a vacuum. The obtained residue is a clear brown liquid of the formula $(\text{OFeX})_3$ [X is linoleate], which dries to a tack-free clear coating upon addition thereto of 0.1 percent (by weight) of cobalt naphthenate.

EXAMPLE 24

Dissolve 10 g of chromic acid in 12 g of acetic acid and 5 g of water. Add 13 g of zinc dust to the resulting solution. A reaction proceeds, as is reflected by a color change from orange-yellow to bright green. Add 84 g of tall oil fatty acids to the resultant and heat same to 220° C. While maintaining that temperature, add 15 g of water thereto followed by 5 g of butanol and then apply a vacuum. The product is the compound of the formula XZnOCr(X)OZnX [X is the residue of tall oil fatty acids] which, when dissolved in mineral spirits, is useful as a preservative stain for wood.

EXAMPLE 25

Stir a mixture of 20 g of chromium trioxide, 10 g of water and 25 g of acetic acid until a clear solution is obtained. Add 10 g of butanol to reduce CrO_3 to chromic oxide (Cr_2O_3) . Add 56 g of isostearic acid to the solution before raising the temperature thereof gradually to 250° C. Water and acetic acid are distilled off. While maintaining the batch at said temperature, add thereto 20 g of water, followed by 20 g of butanol and another 20 g of water. Then apply a vacuum of 2 cm of Hg

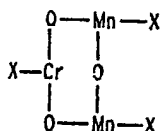
- at the same temperature until distillation ceases (at least 10 minutes). The product is a green solid which is soluble in butanol, xylene and mineral spirits. Solutions in any of these solvents dry to a smooth, high gloss, bright green, transparent coating. Said product is chromic oxide isostearate, predominantly or entirely in cyclic form, i.e. of the formula $(\text{OCrX})_n$, wherein X is isostearate and n is an integer thought to be 3.

Cyclic chromic oxide isostearate is alternatively mixed with linseed oil and alkyd resin to form useful protective coatings.

EXAMPLE 26

- To 5 g of CrO_3 in 10 g of water add 36.8 g of manganese acetate and 56 g of isostearic acid. Heat the resultant mixture gradually to 250°C . Water and acetic acid are distilled off. While maintaining the batch at said temperature (at least 60 minutes), add 20 g of water thereto. Then apply a vacuum of 2 cm of Hg at the same temperature until distillation ceases (at least 10 minutes). The product is a deep brown non-drying liquid which, when mixed with alkyd resin, is useful for producing high-gloss transparent coatings.

The product is of the formula



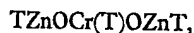
wherein X is isostearate.

EXAMPLE 27

- Stir a mixture of 20 g of CrO_3 , 10 g of water, 25 g of acetic acid and (after reduction with 10 g of butanol) 32.4 g of zinc oxide. Add thereto 119 g of tall oil fatty acids before raising the temperature thereof gradually to 270°C . Water and acetic acid are distilled off. While maintaining the batch at said temperature (at least 60 minutes), add 20 g of water thereto. Then apply a vacuum of 2 cm of Hg at the same temperature until distillation ceases (at least 10 minutes). The product is bright green and is soluble in xylene. It is predominantly of the formula



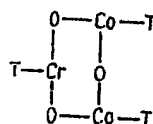
- but may contain some the compound of the formula



- wherein T is the residue of tall oil fatty acids. Xylene solutions of the product dry to clear coatings which are useful as wood preservatives and anticorrosives.

EXAMPLE 28

To 5 g of CrO_3 in 10 g of water add 37.3 g of cobalt acetate and 56 g of tall oil fatty acids. Heat the resultant mixture gradually to 250°C . Water and acetic acid are distilled off. While maintaining the batch at said temperature (at least 60 minutes), add 20 g of water thereto. Then apply a vacuum of 2 cm of Hg at the same temperature until distillation ceases (at least 10 minutes). The product is dark greyish blue and has the formula



wherein T is the residue of tall oil fatty acids.

EXAMPLE 29

Disperse 2.7 g of aluminium powder and 16.2 g of zinc oxide in 30 g of mineral spirits. Add thereto a mixture of 12 g of acetic acid and 56 g of tall oil fatty acids. Heat the resulting mixture. (The batch thickens at 40°C , but melts again at 60°C .) Raise the temperature to 160°C and reflux at that temperature for 60 minutes. Then distill off volatile components as the temperature is increased to 260°C . While maintaining the latter temperature, add 15 g of water to the distilland. Thereafter subject the resultant to a vacuum at the same temperature. The product is of the formula $(\text{TZnO})_2\text{AlOAl}(\text{OZnT})_2$, wherein T is the residue of tall oil fatty acids.

In general any di- or trivalent metal compound reactable with acetic or formic acid can be used in the process illustrated by Examples 8, 9 and 16 to 29. Even minerals, such as metal carbonates, oxides, hydroxides and sulfides, are suited for said process. When both di- and trivalent metals are used to produce a single product, the molar ratio of di- to trivalent metals should be in the range of approximately 2:1.

EXAMPLE 30

Mix 24.7 g of crystalline chromium triacetate with 16.2 g of zinc oxide and add 80 grams of water to the resulting admixture. Heat said admixture at 100°C for 30 minutes, during which time the color thereof changes to dark green. Then add thereto 56 g of tall oil fatty acids and 45 g of mineral spirits. Heat to 220°C . While maintaining this temperature, add 20 g of water to the resultant mixture and then apply a vacuum. The clear green product dissolves in mineral spirits and dries (with 0.5 percent by weight cobalt drier) to a high-gloss clear coating. Said product is of the formula $(\text{TZnO})_2\text{CrOCr}(\text{OZnT})_2$ and may also be used in the same manner as the product of Example 27.

EXAMPLE 31

Heat to 100° C a mixture of 9.5 g of basic iron acetate and 33.5 g of lead oxide with 35 g of water, and maintain at said temperature for 5 minutes. Add 42 g of isostearic acid to the resultant mixture and continue distillation. Add 40 g of mineral spirits gradually to the distilland and raise the temperature to 200° C. While maintaining the latter temperature, add 10 g of water to the distilland and then apply a vacuum thereto. The distilland is a dark brown liquid which solidifies on cooling. The product is of the formula $(XPbO)_2Fe$, wherein X is isostearate.

EXAMPLE 32

Dissolve 120 g of rosin (acid value = 300) in 40 g of mineral spirits and 20 g of acetic acid. Heat the obtained solution to 90° C, and add 32.4 g of zinc oxide thereto at that temperature. Then heat further to 190° C before dropping 25 cubic centimeters (cc) of water slowly thereinto, followed by 15 g of butanol and 20 g of mineral spirits to keep the batch liquid (200° to 230° C). [The smell of butyl acetate is noticeable in the distillate.] Apply a 2 cm of Hg vacuum at 200° C. The product (mp 150° C) dissolves in 50 g of xylene to yield a resinous solution having a zinc content of 16.5 percent (by weight) based on the total solids.

EXAMPLE 33

Add 111.5 g of litharge to a mixture of 74.2 g of 2-ethylhexoic acid, 70 g of acetic acid and 20 g of mineral spirits. Heat the resultant mixture until a clear solution is obtained (150° C). At a temperature between 160° and 210° C add 50 g of butanol to the solution, and maintain in the temperature range for 60 minutes while butyl acetate is slowly distilled off. Apply a vacuum thereafter to obtain 185 g of clear colorless sirupy liquid which is useful as primer for coatings.

Whenever a vacuum is applied throughout the examples, 5 mm Hg are employed unless there is an indication to the contrary.

Although aluminium has been used in some of the Examples as illustrative of the general operability of the process of this invention a preferred class of MAO is that which does not include aluminium among the trivalent metals, aluminium having the lowest atomic weight among the disclosed trivalent metals.

WHAT I CLAIM IS:—

1. A process for preparing a metal oxide acylate by reaction of (a) at least one metal component selected from polyvalent metals and oxides, hydroxides and carbonates thereof, with (b) at least one volatile monocarboxylic acid having from 1 to 5 carbon atoms and (c) at least one monocarboxylic acid having at least 7 carbon atoms to produce a metal oxide acylate wherein at least one valency of each

metal atom derived from the metal component is satisfied by an acylate group and each of the remaining valencies is satisfied either by an oxygen atom which is attached to another metal atom or by an acylate group, which process includes distilling the product at a temperature of from 100 to 250° C, and during the distillation adding a liberating agent for the volatile monocarboxylic acid whereby to liberate said volatile acid and obtain a metal oxide acylate wherein at least 55 mole % of the acylate content is of monocarboxylic acid having at least 7 carbon atoms, the liberating agent being selected from one or more of water, steam, a volatile alcohol, an aluminium alkoxide wherein each alkoxide group has at most four carbon atoms, a titanium alcoholate wherein each alcoholate group has at most four carbon atoms, and a condensed titanium silicon alkoxide wherein each alkoxide group has at most four carbon atoms, the amount of aluminium alkoxide, titanium alcoholate or condensed titanium silicon alkoxide used being not greater than 10% by weight of the metal oxide acylate product.

2. A modification of the process claimed in claim 1 in which the metal component and volatile monocarboxylic acid are replaced by at least one salt of a polyvalent metal and a volatile monocarboxylic acid having from 1 to 5 carbon atoms.

3. A process according to claim 1 or claim 2 wherein each metal element has a valence number of two.

4. A process according to claim 1 or claim 2 wherein each metal element has a valence number of three.

5. A process according to claim 1 or claim 2 wherein each metal element has a valence number of four.

6. A process according to claim 1 or claim 2 wherein a plurality of metal elements are reacted and two of the metal elements differ in their respective valence numbers.

7. A process according to any of claims 1 to 6 wherein the acylate of the metal oxide acylate is entirely that of the monocarboxylic acid having at least 7 carbon atoms.

8. A process according to any of claims 1 to 7 wherein the liberating agent is water or steam or both, and the amount of liberating agent used is sufficient to produce distillate in which the volatile carboxylic acid is no longer noticeable.

9. A process according to any of claims 1 to 7 wherein the volatile alcohol is butanol.

10. A process according to any of claims 1 to 7 wherein the volatile alcohol is isopropanol.

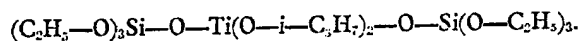
11. A process according to any of claims 1 to 7 wherein the aluminium alkoxide is aluminium butoxide.

12. A process according to any of claims 1 to 7 wherein the aluminium alkoxide is aluminium isopropoxide.

13. A process according to any of claims 1 to 7 wherein the liberating agent is selected from titanium isopropoxide and titanium butoxide.
14. A process as claimed in any of claims 9 to 13 in which the reaction temperature is at least 150° C.
15. A process as claimed in claim 14 in which the reaction temperature is from 170° C to 200° C.
16. A process as claimed in any of claims 1 to 15 in which the molar ratio of metal element to non-volatile monocarboxylic acid in the reaction mixture is in excess of 1:1.
17. A process according to claim 16 wherein the molar ratio is 2:1.
18. A process according to claim 16 wherein the molar ratio is 3:1.
19. A process as claimed in any of claims 1 to 18 in which the volatile monocarboxylic acid is acetic acid.
20. A process as claimed in any of claims 1 to 19 in which the monocarboxylic acid having at least 7 carbon atoms is selected from stearic acid, isostearic acid, oleic acid, linoleic acid, 2-ethyl-hexanoic acid and tall oil fatty acids.
21. A process as claimed in claim 1 or claim 2, substantially as hereinbefore described and as shown in the Examples.
22. A metal oxide acylate obtained by a process claimed in any of claims 1 to 21.
23. A metal oxide acylate having at least two metal atoms other than aluminium bound to each other through an oxygen bridge and which has a formula selected from
- $$\begin{array}{c} \text{XMOMX} \\ \text{XMOM''(X)}_2\text{OMX} \\ \text{X}_2\text{M'OM''(X)}_2\text{OM'X}_2 \end{array} \quad \text{and}$$
- where each X is an acylate group, each M is a divalent metal atom, each M' is a trivalent metal atom and each M'' is a tetravalent metal atom, and at least 55 mole % of the total acylate content of the compound is derived from carboxylic acid having at least 7 carbon atoms, the remainder if any being derived from carboxylic acid having less than 7 carbon atoms.
24. A metal oxide acylate as claimed in claim 23 in which each M is selected from Fe^{II}, Cu^{II} and Zn; each M' is selected from Cr^{III} and Fe^{III} and each M'' is selected from Ti^{IV} and Zr^{IV}.
25. A metal oxide acylate as claimed in claim 23 or claim 24 which is virtually or entirely free of acylate groups derived from volatile monocarboxylic acids having 1 to 5 carbon atoms.
26. A metal oxide acylate according to claim 23 or claim 24 wherein the metal comprises at least two metals of different valence numbers and at least 70 mole percent of the acylate content is derived from monocarboxylic acid having at least 7 carbon atoms.
27. Copper oxide tallate having this structure TCuOCuT where each T represents an acylate of a tall oil fatty acid.
28. Ferric oxide tallate having the structure (OF₂T)₂ where each T represents an acylate of a tall oil fatty acid.
29. A compound having the structure (XMgO)₂AlOAl(OMgX)₂ where X is stearate.
30. A compound having the structure (TZnO)₂CrOCr(OZnT)₂ where each T represents an acylate of a tall oil fatty acid.
31. A compound of the formula (XPbO)₃Fe where X is isostearate.
32. A composition which comprises a metal oxide acylate having at least two metal atoms other than aluminium bound to each other through an oxygen bridge and in which each metal atom has a valence number of at least two and is bound only to oxygen atoms and at least 55 mol percent of the acylate content is derived from monocarboxylic acid having at least 7 carbon atoms, the remainder of the acylate if any being derived from monocarboxylic acid having less than 7 carbon atoms the molar ratio of metal to acylate in the composition being in excess of 1:1, and the excess metal being in a finely divided, stable, dispersed state as metal oxide.
33. A colored composition according to claim 32 which consists essentially of said excess metal dispersed as oxide in the metal oxide acylate.
34. A composition according to claim 33 wherein the metal of the metal oxide acylate is ferric iron.
35. A composition according to claim 33 wherein the metal of the metal oxide acylate is ferrous iron.
36. A composition according to claim 33 wherein the metal of the metal oxide acylate is copper.
37. A composition according to claim 33 wherein the metal of the metal oxide acylate is chromium.
38. A composition according to claim 33 wherein the metal of the metal oxide acylate is nickel.
39. A composition according to claim 33 wherein the metal of the metal oxide acylate is manganese (III).
40. An imitation gold paint which consists essentially of an admixture of aluminium flake and ferric oxide tallate.
41. A liquid (metal oxide acylate)/(metal alkoxide) reaction product, the metal oxide acylate having at least two metal atoms other than aluminium bound to each other through an oxygen bridge and in which each metal atom has a valence number of at least two and is bound only to oxygen atoms and at least 55 mol percent of the acylate content is derived from monocarboxylic acid having at least 7 carbon atoms the remainder of the acylate if any being derived from monocarboxylic acid having less than 7 carbon atoms,

the metal alkoxide comprising at most 10 percent by weight based on the weight of said metal oxide acylate and being selected from the group consisting of aluminium alcoholate, titanium alcoholate and condensed titanium silicon alkoxide.

42. A reaction product according to claim 41 wherein the metal of the metal oxide acylate is zinc, the acylate is that of ethylhexoic acid, and the metal alkoxide is the compound of the formula



43. A metal oxide acylate as claimed in claim 23 or a composition as claimed in any one of claims 32, 40 or 41, substantially as hereinbefore described and as shown in the Examples.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of)	
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BARROW <i>et al.</i>)	Art Unit: Unassigned
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International Application No. PCT/IB06/001526)	
)	Confirmation No. Unassigned
US National Phase Filing Date: April 10, 2006)	
International Filing Date: January 26, 2006)	
)	
For: CHROMIUM-FATTY ACID COMPOUNDS AND)	
METHODS OF MAKING AND USING THEREOF)	

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

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NEEDLE & ROSENBERG, P.C.
Customer Number 23859

January 17, 2007

Sir:

Pursuant to the requirements of 37 C.F.R. § 1.56, submitted herewith on the accompanying Information Disclosure Statement List is a listing of documents known to Applicants and/or their attorneys. In accordance with 37 C.F.R. §1.98(a)(2), copies of any cited U.S. patent or U.S. patent application publication documents are not enclosed. Copies of any cited foreign patent document and/or any non-patent publication are enclosed.

This Information Disclosure Statement is believed to be filed in a timely manner pursuant to 37 C.F.R. § 1.97(b)(3), in that a first Office Action on the merits of the present patent application has not yet been mailed to Applicants.

Consideration of the cited documents and making the same of record in the prosecution in the above-referenced application are respectfully requested.

ATTORNEY DOCKET NO. 15113.0007U2
Application No. 10/575,204

No fee is believed due; however, the Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 14-0629.

Respectfully submitted,

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